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14. ABSTRACT
The work performed under this proposal was primarily that by Professor Eric Pop. Professor Pop left Illinois for a faculty position at Stanford, at which point Professor Joseph Lyding took over as Illinois PI. Professor Lyding helped manage the Pop group remaining at Illinois after Professor Pop left, and he engaged in a collaborative effort with the Pop group to develop a selective thermal treatment process to improve the performance of carbon nanotube array transistors. Such transistors suffer about two orders of magnitude performance penalty due to high nanotube-nanotube resistances in the current pathways from source to drain. Thus, under normal operation CNT array

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UU	UU	UU	UU		Joseph Lyding
					19b. TELEPHONE NUMBER
					217-333-8370

Report Title

Final Report: Energy Guiding and Harvesting through Phonon-Engineered Graphene

ABSTRACT

The work performed under this proposal was primarily that by Professor Eric Pop. Professor Pop left Illinois for a faculty position at Stanford, at which point Professor Joseph Lyding took over as Illinois PI. Professor Lyding helped manage the Pop group remaining at Illinois after Professor Pop left, and he engaged in a collaborative effort with the Pop group to develop a selective thermal treatment process to improve the performance of carbon nanotube array transistors. Such transistors suffer about two orders of magnitude performance penalty due to high nanotube-nanotube resistances in the current pathways from source to drain. Thus, under normal operation CNT array transistors dissipate most of their energy at the inter-nanotube junctions. We developed an approach, termed nanosoldering that uses joule heat-ing to selectively metallize the nanotube-nanotube junctions thereby reducing junction resistance and improving overall device characteristics.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
05/10/2012	3.00	Cheng-Lin Tsai, Albert Liao, Eric Pop, Moonsub Shim. Electrical power dissipation in semiconducting carbon nanotubes on single crystal quartz and amorphous SiO2, Applied Physics Letters, (08 2011): 53210. doi: 10.1063/1.3622769
05/10/2012	2.00	Albert Liao, Justin Wu, Xinran Wang, Kristof Tahy, Debdeep Jena, Hongjie Dai, Eric Pop. Thermally Limited Current Carrying Ability of Graphene Nanoribbons, Physical Review Letters, (06 2011): 256801. doi: 10.1103/PhysRevLett.106.256801
05/10/2012	1.00	Myung-Ho Bae, Feifei Lian, Eric Pop, William P. King, Kyle L. Grosse. Nanoscale Joule heating, Peltier cooling and current crowding at graphene–metal contacts, Nature Nanotechnology, (04 2011): 287. doi: 10.1038/nnano.2011.39
05/10/2012	5.00	Zhun-Yong Ong, Eric Pop. Effect of substrate modes on thermal transport in supported graphene, Physical Review B, (08 2011): 75471. doi: 10.1103/PhysRevB.84.075471
05/10/2012	4.00	David Estrada, Eric Pop. Imaging dissipation and hot spots in carbon nanotube network transistors, Applied Physics Letters, (02 2011): 73102. doi: 10.1063/1.3549297
05/11/2012	6.00	Sharnali Islam, Vincent E. Dorgan, Eric Pop, Myung-Ho Bae. Scaling of High-Field Transport and Localized Heating in Graphene Transistors, ACS Nano, (10 2011): 7936. doi: 10.1021/nn202239y
09/23/2012	8.00	Kevin T. He, Joshua D. Wood, Gregory P. Doidge, Eric Pop, Joseph W. Lyding. Scanning Tunneling Microscopy Study and Nanomanipulation of Graphene-Coated Water on Mica, Nano Letters, (06 2012): 2665. doi: 10.1021/nl202613t
09/23/2012	12.00	Ashkan Behnam, Austin S. Lyons, Myung-Ho Bae, Edmond K. Chow, Sharnali Islam, Christopher M. Neumann, Eric Pop. Transport in Nanoribbon Interconnects Obtained from Graphene Grown by Chemical Vapor Deposition, Nano Letters, (09 2012): 4424. doi: 10.1021/nl300584r
11/14/2013	14.00	Sharnali Islam, Zuanyi Li, Vincent E. Dorgan, Myung-Ho Bae, Eric Pop. Role of Joule Heating on Current Saturation and Transient Behavior of Graphene Transistors, IEEE Electron Device Letters, (02 2013): 0. doi: 10.1109/LED.2012.2230393
11/14/2013	15.00	Andrey Y. Serov, Zhun-Yong Ong, Eric Pop. Effect of grain boundaries on thermal transport in graphene, Applied Physics Letters, (01 2013): 0. doi: 10.1063/1.4776667
11/14/2013	13.00	Ashkan Behnam, Vinod K. Sangwan, Xuanyu Zhong, Feifei Lian, David Estrada, Deep Jariwala, Alicia J. Hoag, Lincoln J. Lauhon, Tobin J. Marks, Mark C. Hersam, Eric Pop. High-Field Transport and Thermal Reliability of Sorted Carbon Nanotube Network Devices, ACS Nano, (01 2013): 0. doi: 10.1021/nn304570u
11/14/2013	16.00	Myung-Ho Bae, Zuanyi Li, Zlatan Aksamija, Pierre N Martin, Feng Xiong, Zhun-Yong Ong, Irena Knezevic, Eric Pop. Ballistic to diffusive crossover of heat flow in graphene ribbons, Nature Communications, (04 2013): 0. doi: 10.1038/ncomms2755

TOTAL: 12

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

1. J.-W. Do, D. Estrada, X. Xie, N. Chang, J. Mallek, G. Girolami, J. Rogers, E. Pop, and J. W. Lyding, "Self-Limiting and Selective Nanosoldering of Carbon Nanotube Junctions for Im-proved Device Performance", International Conference on Nanoscience and Technology, Ju-ly 2014.
2. J.-W. Do, D. Estrada, X. Xie, N. Chang, J. Mallek, G. Girolami, J. Rogers, E. Pop, and J. W. Lyding, "Self-Limiting and Selective Nanosoldering of Carbon Nanotube Junctions for Im-proved Device Performance", Materials Research Society Spring Meeting, April 2014.

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received		Paper
01/28/2016	17.00	Jae-Won Do, Noel N. Chang, David Estrada, Feifei Lian, Hyeongyun Cha, Xiangyun J. Duan, Richard T. Haasch, Eric Pop, Gregory S. Girolami, Joseph W. Lyding. Solution-Mediated Selective Nanosoldering of Carbon Nanotube Junctions for Improved Device Performance, ACS Nano (05 2015)
09/23/2012	9.00	Eric Pop, Vikas Vashney, Ajit K. Roy. Thermal properties of graphene:Fundamentals and applications, MRS Bulletin (04 2012)
09/23/2012	10.00	Myung-Ho Bae, Zuanyi Li, Zlatan Aksamija, Pierre N. Martin, Feng Xiong, Zhun-Yong Ong, Irena Knezevic, Eric Pop. Ballistic to diffusive crossover of heat flow in graphene ribbons, Nature Nanotechnology (submitted) (08 2012)
09/23/2012	11.00	Sharnali Islam, Zuanyi Li, Vincent E. Dorgan, Myung-Ho Bae, Eric Pop. Role of Joule Heating on Current Saturation and Transient Behavior of Graphene Transistors, IEEE Electron Device Letters (submitted) (01 2012)

TOTAL: **4**

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Jae Won Do	1.00	
FTE Equivalent:	**1.00**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Jae Won Do

Total Number: **1**

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

Scientific Progress:

Solution-Mediated Selective Nanosoldering of Carbon Nanotube Junctions for Improved Device Performance

J-W. Do, N.N. Chang, D. Estrada, F. Lian H. Cha X.J. Duan, R.T. Haasch, E. Pop, G.S. Girolami, J.W. Lyding , *ACS Nano* vol. 9, p. 4806 (2015).

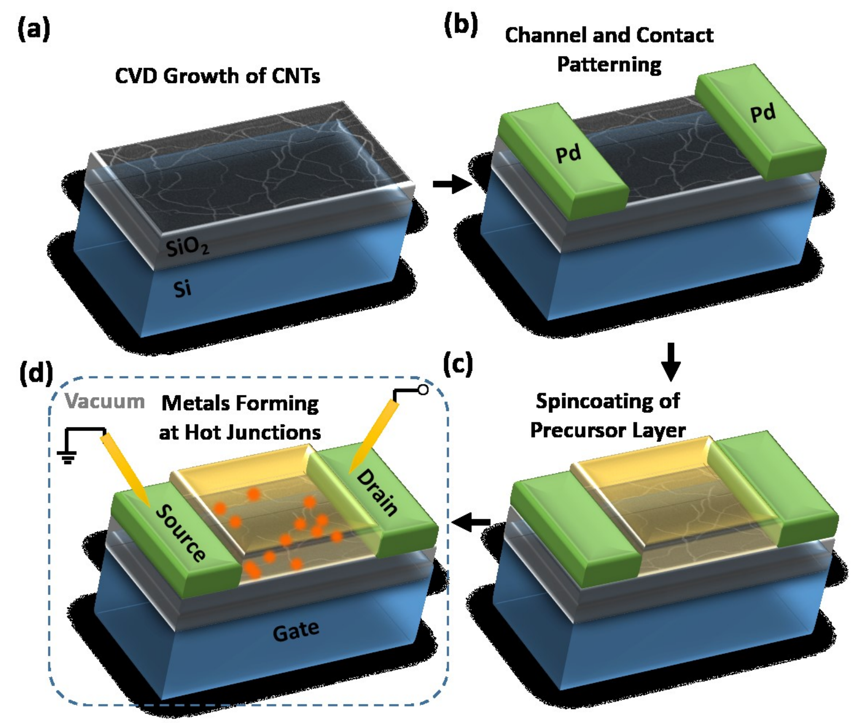

Figure 1. Schematic diagrams of **(a)** carbon nanotube (CNT) network growth on a SiO_2/Si substrate by chemical vapor deposition (CVD), **(b)** device fabrication using standard photolithography and e-beam evaporation for channel and contact patterning with Ti/Pd (0.5/40 nm) electrodes, **(c)** solution-mediated application of the $Pd_2(dba)_3$ precursor onto CNT networks by spincoating, and **(d)** selective Pd deposition triggered by resistive heating at CNT junctions under device operation in vacuum probe station.

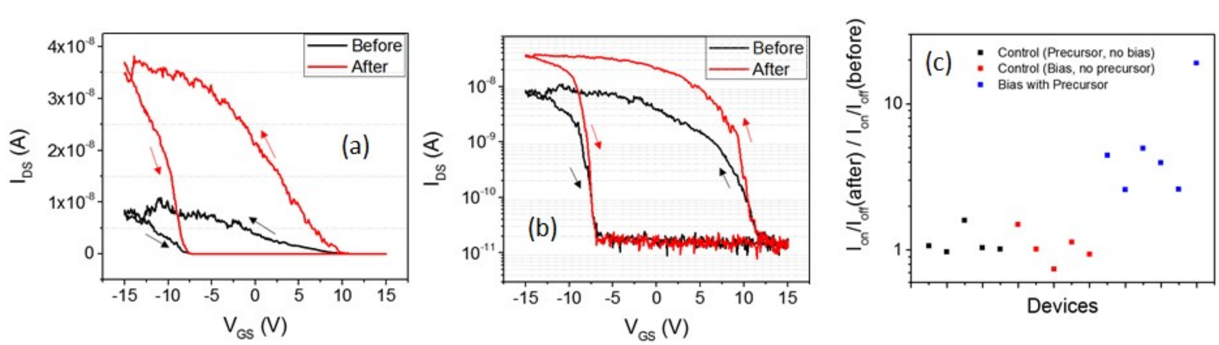

Figure 2. (a) Linear, and (b) log transfer characteristics of a CNT network device before and after Pd deposition in (left) linear and (right) log scales with $V_{DS} = 1$ V. The arrows indicate V_{GS} sweep direction. Channel length and width are $L = 150$ µm and $W = 50$ µm, respectively for both devices. (c) Summaries of improvement in I_{ON}/I_{OFF} ratios upon control experiment with precursor but no bias (black), with bias but no precursor (red), and upon Pd deposition with precursor and bias (blue).

The specific nature of the nanosoldering process is to use joule heating to drive local CVD reactions at the hot nanotube-nanotube junctions. During metal deposition the junction resistance drops, which causes the junctions to cool, thus stopping further metal deposition. The nice simplicity about the nanosoldering process is it's self-aligned, self-limiting behavior.

Initial studies performed in a vacuum CVD system achieved up to a factor of ~8 improvement in CNT array FET performance, using palladium metallization. An important development in this work was to replace the vacuum CVD process with one based on a spin coated layer of CVD precursor. This is depicted in figure 1 for CNTs grown by CVD on SiO_2. After CNT growth,

Pd source and drain contacts are fabricated, followed by deposition of a Pd precursor. The specific precursor that we used is $Pd_2(dba)_3$, where dba stands for dibenzoylacetone. This precursor is frequently used as a Pd CVD source, however it is also soluble in common solvents such as chloroform, thus making it suitable for spin coating applications.

Control experiments were performed in which it was observed that the device transfercharacteristics we not changed by the spin coated $Pd_2(dba)_3$ layer. In the control experiment the coated device substrate was transferred into the vacuum probe station where nanosoldering is performed and then removed without performing the nanosoldering step. The spin coated layer was then removed and the device transfer characteristics measured.

Figure 2 shows the resultant change in the transfer characteristics when the nanosoldering step is inserted. Approximately a factor of 5 improvement in I_{ON} is observed after nanosoldering. Figure 2c shows the changes in the I_{ON}/I_{OFF} ratio for six devices subjected to nanosoldering. Control experiment results are also presented where no significant change is observed.

In addition to electrical characterization, SEM imaging and energy dispersive x-ray spectroscopy (EDS) experiments were performed. Figure 3 shows SEM images of a nanosoldered and control devices. In the nanosoldered device, white deposits are observed at some of the nanotube junctions. Figure 3j shows EDS spectra that indicate that the deposits are Pd metal.

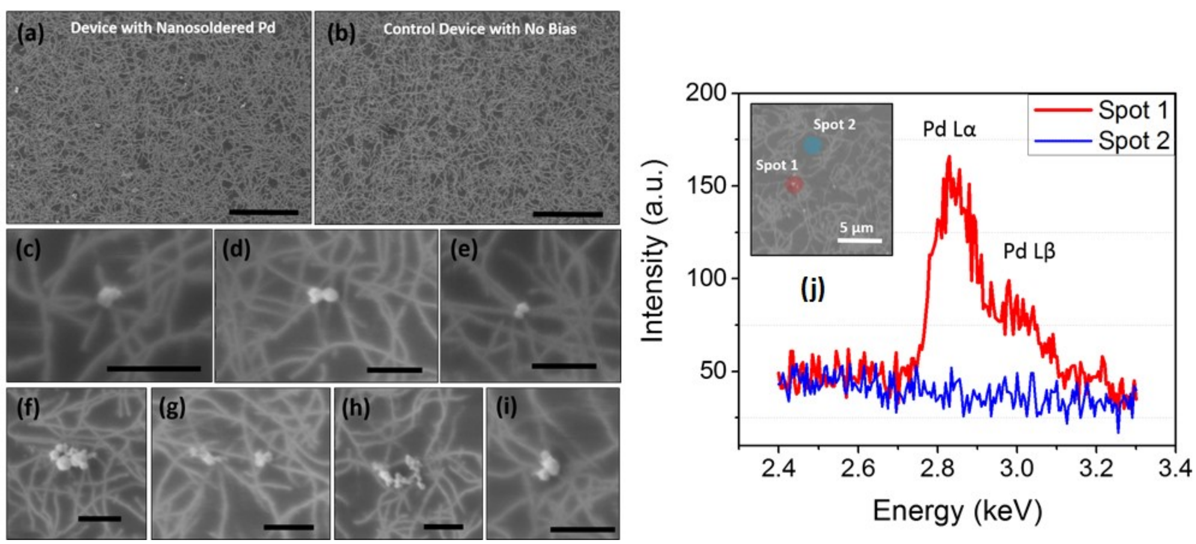

Figure 3. (a) A scanning electron microscope (SEM) image of a CNT network after Pd deposition. Scale bar is 5 μm. **(b)** An SEM image of a control device where precursor was applied without any current flow, showing no noticeable Pd particles or residues. Scale bar is 5 μm. **(c-i)** Zoomed-in SEM images of CNT network showing CNT junctions nanosoldered with Pd particles. The scale bar is 1 μm. (j) EDS spectrum from a CNT network after Pd deposition. The red curve is collected from spot 1 and the blue curve is collected from spot 2 in the inset SEM image, corresponding to bright particles at carbon nanotube junctions and on bare SiO_2 surface, respectively. The EDS data indicate that the deposited material is Pd.